

**929.** *The Effects of Crystal Fields on the Properties of Transition-metal Ions.*

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The properties of the ions of the transition metals are discussed in terms of Schlapp and Penney's theory of crystal fields (*Phys. Review*, 1932, **42**, 666). Attention is drawn to the general similarity of the crystal-field theory and Pauling's theory of covalent and ionic bonds ("The Nature of the Chemical Bond," New York, 1945). It is shown that the heats of hydration, the magnetic and optical properties, and the stereochemistry of certain transition-metal compounds can be interpreted in terms of crystal-field theory.

In discussions of the chemical and physical properties of the compounds of the transition metals two apparently different approaches are possible. One may adopt either Pauling's theory of ionic and covalent bond types ("The Nature of the Chemical Bond," New York, 1945, Chapter III) or Schlapp and Penney's theory of crystal fields (*Phys. Review*, 1932, **42**, 666) which is the basis of most of the detailed magnetic studies (Abragam and Pryce, *Proc. Roy. Soc.*, 1951, **205**, A, 135). It is the object of this paper to illustrate the qualitative similarity of the theories and to show how the crystal-field formulation may be used to interpret the heats of hydration, magnetic behaviour, optical absorption, and stereochemistry of the transition-metal ions.

The essential physical idea of the crystal-field theory is that the electrons of a central ion tend to avoid those regions where the field due to the attached negative ions and dipoles is largest. This tendency may result in the removal of the degeneracy of the ground state of certain transition-metal ions: thus the set of *d*-orbitals in a field due to a regular octahedron of negative ions or dipoles is split into two levels, a lower triplet  $T_2$  and an upper doublet *E*. The triplet of orbitals corresponds to a high electron density between the lines joining the centre to the vertices of the octahedron, the doublet to a high density along these lines. For a single *d*-electron the lower level will be occupied but the position of the upper level can be found from the visible or infra-red spectrum which gives the energy difference. It will be shown that the connection between this theory and Pauling's orbital theory follows from the properties which an ion develops in an electric field. As a result of the spatial shift of electronic charge, the electronegativity becomes dependent on the direction, being greatest in the direction of attached negative groups and least between these directions, where the shielding is greatest.

In the case of more than one electron in a cubic field the tendency of electrons to accumulate between the bonding directions is opposed by the electrostatic repulsions between electrons. The properties of the ion now depend more critically on the strength of the field.

*Weak Fields.*—If the cubic field is weak compared with these repulsions it may be shown that its effect is to cause a splitting of the ground state of the ion provided this is not an S state. Compounds for which this assumption is true prove to have magnetic properties which would cause them to be classified by Pauling's theory as ionic compounds.

One advantage of the crystal-field theory is that it does allow us to calculate the stabilisation of these complexes owing to the splitting of the ground-state degeneracy.

Energy-level diagrams for this splitting are given in the literature (Schlapp and Penney, *loc. cit.*). A typical example is that shown for  $\text{Ni}^{++}$  in Fig. 1. The stabilisation of this ion in its hydrated salts corresponds to the distance  $I$  in the diagram. This and similar quantities for the other hydrated ions can be estimated from the infra-red and visible spectra of solutions (Bose and Mukherji, *Phil. Mag.*, 1938, **26**, 757; Dreisch, *Z. phys. Chem.*, 1937, **37**, B, 40; 1939, **45**, B, 26). In Table 1 we give the heats of hydration of the bivalent ions of the first long period (Quill, "The Chemistry and Metallurgy of Miscellaneous Materials: Thermodynamics," New York), the estimated stabilisation energies to the nearest 5 kcals., and the differences, *i.e.*, the estimated hydration energies in the absence of the cubic-field splitting. It will be seen that the anomalous heat of hydration of  $\text{Mn}^{++}$  with an  $S$  ground state is thus removed. The increase in the hydration energy with the completion of the  $3d$  shell up to  $\text{Zn}^{++}$  is as one would expect.

This explanation of the heats of hydration of the bivalent ions is confirmed by the values of the heats of hydration of the trivalent ions. The ion with an  $S$  ground state is now

FIG. 1. The splitting of the  ${}^3F$  ground state of  $\text{Ni}^{++}$  in a field of cubic symmetry.

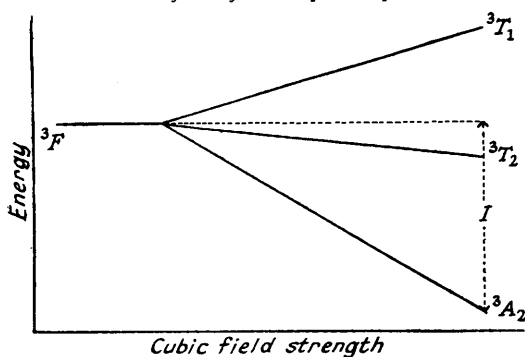
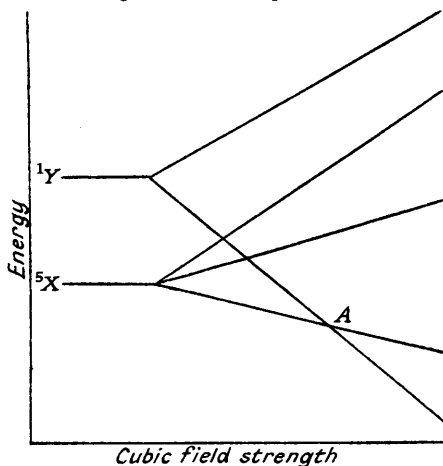


FIG. 2. Diagrammatic representation of the displacement of a diamagnetic state below the normal paramagnetic ground state showing the transition point A.



$\text{Fe}^{+++}$ . The heats of hydration of  $\text{Cr}^{+++}$ ,  $\text{Mn}^{+++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Co}^{+++}$  are 1093, 1111, 1059, and 1141, respectively,  $\text{Fe}^{+++}$  being anomalously low.

The connection between the overall stability and the crystal-field splitting is much more complicated since the component of the field causing the splitting is small compared with the terms responsible for the binding and also because it takes no account of steric factors,

TABLE 1.

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Heat of hydrtn. ....	426	453	460	445	468	497	507	507	491
Stabilisation .....	—	35	20	0	10	20	25	20	0
Difference .....	—	418	440	445	457	477	482	487	491

etc. Inferences from spectral absorption to thermochemical stability are therefore very speculative, particularly if different types of ligand, say ions and neutral dipoles, are being compared. Within a given series, however, it does seem probable that larger crystal-field splittings and hence higher absorption frequencies will usually be associated with stronger bonding.

*Strong Fields.*—If the cubic field becomes greater than a certain critical value it may displace a level of lower spin multiplicity below the normal ground state. This is shown diagrammatically in Fig. 2. In such cases there will be a discontinuous change in the magnetic susceptibility when the energy levels cross. In  $\text{Co}^{+++}$ , for example, a singlet level may be displaced below the various components into which the  ${}^5F$  ground state of

the free ion is split. If the field becomes very strong it may be a good approximation to consider the new ground state of  $\text{Co}^{+++}$  as arising from the occupation of the lower triplet of orbitals by six electrons. This corresponds almost exactly to Pauling's picture of two bonding  $d$ -orbitals and three occupied non-bonding orbitals, since the empty doublet is directed towards the ligands and hence these are placed in a strong polarising field, while the occupied triplet of orbitals is practically non-polarising, *i.e.*, non-bonding. In fact, the crystal fields operating in most of these compounds are of intermediate strength.

It must be emphasized that it is not true that complete breakdown of the normal L-S coupling scheme is necessary before the nature of the ground state is changed. The size of the cubic field required in  $\text{Co}^{+++}$ , for instance, will depend on the nature and position of the lowest singlet state, and in general will depend on the electronic structure of the ion concerned.

It should be noted that, at the point at which the magnetic properties of the ion change discontinuously, there is no discontinuous change in the stabilisation energy, although the rate of change of this quantity with field strength certainly increases. This implies that we must not expect all "covalent" bonds to be stronger than "ionic" bonds. Taube (*Chem. Reviews*, 1952, 50, 69) has drawn attention to the fact that it is the lability of complexes rather than their thermochemical stability which is closely related to electronic structure.

The spectroscopic properties of the complexes will clearly change discontinuously with the change in the nature of the ground state owing to the different selection rules. In this connection it is interesting that the spectra of the complexes of  $\text{Cr}^{+++}$  and  $\text{Co}^{+++}$  are very similar. Now,  $\text{Cr}^{+++}$  has a  ${}^4F$  ground state and  $\text{Co}^{+++}$  a  ${}^5D$  ground state, so no explanation in terms of the free ions is possible. If we assume that we are dealing with fairly strong fields, however, the explanation becomes clear. In each case we are removing an electron from the lower orbital triplet and exciting it to the doublet. Four levels are obtained in this way, only two of which have the same spin multiplicity as the ground state. We assume that the two long wave-length absorptions of  $\text{Cr}^{+++}$  and  $\text{Co}^{+++}$  correspond to these allowed transitions. A simple perturbation theory calculation shows that, expressed in Slater-Condon parameters (Condon and Shortley, "Theory of Atomic Spectra," Cambridge, 1935), the separation between the two levels is  $12(F_2 - 5F_4)$ . This corresponds to a frequency separation of about  $10,500 \text{ cm}^{-1}$ . The observed separations between the maxima of the two absorption bands in  $[\text{Co}(\text{NH}_3)_6]^{+++}$  and  $[\text{Cr}(\text{NH}_3)_6]^{+++}$  are about  $8500$  and  $6900 \text{ cm}^{-1}$ , respectively (Linhard and Weizel, *Z. anorg. Chem.*, 1951, 266, 49).

Calculations of the effect of an axial field on the two levels (see Appendix, p. 4760) show that the lower excited state breaks up into a doublet and a singlet, while the upper state is not split in the first approximation. It is found experimentally that in the mono-substituted cobaltamines and chromamines the first absorption band is often split but the second is not. This gives some support to the qualitative aspects of the theory.

The relative magnitudes of the cubic-field effect and the inter-electronic repulsions can be estimated from the absorption spectra if the atomic spectrum is known. In  $\text{V}^{+++}$  the free ion has only two low-lying triplet states, a  ${}^3F$  ground state and a  ${}^3P$  state  $13,000 \text{ cm}^{-1}$  above it ("Atomic Energy Levels," National Bureau of Standards, Washington, 1949). The hydrated ion has two absorption bands at  $17,000$  and  $25,000 \text{ cm}^{-1}$  (Furman and Garner, *J. Amer. Chem. Soc.*, 1950, 72, 1785). The calculated energy-level diagram is shown in Fig. 3. The full lines represent the calculated energy levels as a function of the cubic-field strength. The dotted lines are the corresponding levels on the weak-field approximation. It will be seen that, if we can associate the two observed bands with the two lowest transitions on the calculated energy-level diagram, then the cubic-field strength is of the same order of magnitude as the inter-electronic repulsions. The agreement between the observed and calculated frequencies is not very good, the observed difference being about  $8000 \text{ cm}^{-1}$  and that calculated about  $11,000 \text{ cm}^{-1}$ .

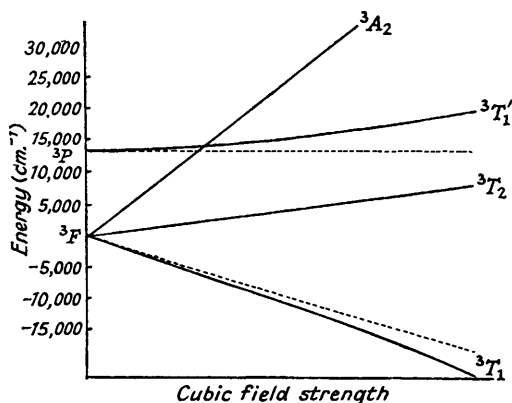
In order to compare the Pauling and the Penney and Schlapp theory we must remember that in the latter the cubic-field strength is determined by the charges, dipole moments, and particularly by the polarisabilities of the ligands. Since also the polarisability of the

ligands may be equated almost directly with the covalent character of the bonds, the connection with the former theory is obvious. However, we now see that the magnetic character of a complex does not distinguish between very covalent and very ionic bonds but, roughly, acts as an indicator showing whether the covalent character has passed a certain limiting value, this value being different for each metal ion and depending on its electronic structure rather than on the polarity of the bonds it forms. Incidentally, a polarisable ligand tends to modify the central ion in such a way as to increase its polarisation.

Another factor which may affect the splitting between the doublet and triplet of orbitals is double-bonding. Orbitals of the lower triplet have the correct symmetry to combine with  $\pi$ -orbitals of attached groups. This will result in a further lowering of the triplet with respect to the doublet and also in some reduction of inter-electronic repulsions. Both of these factors favour the ground states of low multiplicity.

We must now consider the non-octahedral complexes of the transition-metal ions. In the tetrahedral complexes the theory shows that the cubic-field splitting has the opposite sign to that with which we have already dealt, *i.e.*, tetrahedrally disposed negative charges have the same effect on the energy levels as octahedrally disposed positive charges. This

FIG. 3. Energy-level diagram for  $V^{+++}$ . Broken lines are based on the weak-field approximation; full lines on intermediate-field theory. The cubic-field strength is given in terms of the quantity  $A$  defined in the Appendix.



difference will result in a complete change in the absorption spectrum and in the detailed magnetic properties. The difference in colour between the red octahedral complexes of  $Co^{+2}$  and the blue tetrahedral complexes may arise in this way.

The formation of planar complexes can be explained in the crystal-field theory in a way similar to that used by Pauling. If more than six electrons are present in the  $d$ -shell of an ion, then even in strong cubic fields at least one electron must occupy the upper doublet. A deformation of the octahedron leading to expansion along one diagonal and contraction in the two directions at right angles leads to a further splitting of the degenerate energy levels. Complete removal of two groups leaving a planar complex leads, in the first approximation, to two lower doublets and an upper singlet. As in Pauling's scheme, these orbitals are occupied to the best advantage by just eight electrons in the two doublets. In addition, some stabilisation is obtained for 7- and 9-electron systems. A theoretical treatment shows that for 8-electron systems the octahedral and planar configurations are both stable, but that in the other systems the perfect octahedral structure cannot be stable because of a Jahn-Teller effect (Van Vleck, *J. Chem. Phys.*, 1939, 7, 61, 72). It seems possible that the unusual stereochemistry of  $Cu^{++}$  with four planar and two more distant neighbours may be connected with this effect. In the usual covalent-bond theory the stereochemistry of  $Cu^{++}$  is not easily explained. If the  $4d$ -orbitals are used we would expect octahedral  $sp^3d^2$  bonding; if the bonding is  $dsp^2$  then the resistance to oxidation seems inconsistent with the presence of an unpaired  $4p$ -electron.

The physical basis of the extra stability of the non-octahedral complexes is most easily seen from simple electrostatics. In  $Cu^{++}$  there is just one half-empty orbital in the  $d$ -shell. It will clearly be most advantageous to make this coincide with a position of high electron

density of the ligands. If four of the ligands in one plane move closer to the central ion and the other two move away, then a plane of high density is formed with a lower electron density in a direction perpendicular to it. If now the half-empty orbital moves into this plane of high electron density there may be a stabilisation of the complex relatively to the undistorted octahedral form. The extent of the deformation will depend on the relative magnitudes of the electronic stabilisation and the energy needed to produce small deformations of the octahedron in the absence of the electronic effect. In  $\text{Ni}^{++}$  the energy of the ground state is not affected by a distortion of the type discussed above since, of the two half-empty orbitals, one is stabilised and the other destabilised to the same extent. However, there is an excited state with one completely empty orbital which is very strongly stabilised by distortion, and it is this state which is responsible for the diamagnetic planar complexes of  $\text{Ni}^{++}$ .

Finally, we discuss the lability of complex ions. As Taube (*Chem. Reviews*, 1952, 50, 69) points out, this depends far more on the electronic type of the central ion than on the heat of formation of the complex. Experimentally, it is found that the "covalent" complexes with more than three  $d$ -electrons are non-labile while most other complexes react very quickly. The cubic-field theory is not able to add anything to the suggestion that this depends on the presence of an empty  $d$ -orbital available for bonding in the transition state. However, the interpretation is perhaps a little more detailed. In the field due to an approaching charge or dipole, the non-bonding triplet of orbitals is split, the orbital directed towards the approaching group being least stable. If only one or two electrons are present then it is possible to leave this orbital vacant in the ground state without changing the spin multiplicity. In this case the approaching ligand will be in a highly polarising field and hence will be "partially bonded" in the transition state. If three or more electrons are present in the  $d$ -shell, then the shielding of the approaching group is much stronger than that of the six ligands already attached to the central ion, and hence a high energy will be needed to reach a state where all seven groups are approximately equivalent. Hence the activation energy will be high, thus explaining the non-labile character of these complexes.

#### *Appendix.*

The theory of the effect of small crystal fields on the properties of paramagnetic ions has been treated fully in the literature, references to which have already been given. While the theory for the case of the strong field is quite straightforward it does not seem to have been discussed, so it is desirable to outline the methods used in this paper.

The effect of a cubic field on the set of  $d$ -orbitals splits it into a lower triplet spanned by the orbitals

$$a = \frac{1}{\sqrt{2}} (|1\rangle + |-1\rangle), \quad b = \frac{1}{\sqrt{2}} (|1\rangle - |-1\rangle), \quad c = \frac{1}{\sqrt{2}} (|2\rangle - |-2\rangle)$$

and an upper doublet spanned by

$$d = |0\rangle \qquad e = \frac{1}{\sqrt{2}} (|2\rangle + |-2\rangle)$$

where  $|n\rangle$  is the  $d$ -orbital with  $L_z = n$ . The triplet transforms as  $T_2$  and the doublet as  $E$ , the usual notation being used for the octahedral group.

The different configurations of the ion now arise from the different distributions of the electrons in  $T_2$  and  $E$  orbitals. The different states of the ion are now classified according to the representations of the octahedral group. The types of level arising from a given configuration are easily found by forming the appropriate product representation and then decomposing this into irreducible representations in the usual way.

To the first order the energy for the appropriate eigen-functions is then calculated in terms of Slater-Condon parameters just as for free atoms. To obtain a better estimate of the energies we can carry out a second-order perturbation theory calculation, using the inter-electronic repulsions as the perturbation. The case of the intermediate field can be

treated equally well as a perturbation problem on the free ion or as a perturbation problem on the strong-field model.

In this paper we have been interested in the spin triplet states arising from the configuration  $d^2$  of the free ion and in certain states of the configurations  $d^3$  and  $d^6$ . The only calculations needed concerned the  $d^2$  configuration.

The ground state of  $d^2$  in the strong-field approximation may be written as  $(T_2)^2$ . It gives rise to a triplet state  ${}^3T_1$ . The first excited configuration is  $(T_2)^1(E)^1$  which gives two triplets  ${}^3T_1^1$  and  ${}^3T_2$ . The only other triplet state is the  ${}^3A_2$  arising from the configuration  $(E)^2$ . The eigen-functions for the  $T_1^1$  and  $T_2$  states are:

$$\begin{array}{lll} T_1^1 \text{ Det}|ce|, & \text{Det}|\frac{1}{2}b(\sqrt{3}d - e)|, & \text{Det}|\frac{1}{2}a(\sqrt{3}d + e)| \\ T_2 \text{ Det}|cd|, & \text{Det}|\frac{1}{2}b(d + \sqrt{3}e)|, & \text{Det}|\frac{1}{2}a(d - \sqrt{3}e)| \end{array}$$

The other eigen-functions are obvious. The electronic energies of the various states are (apart from a constant term)

$$\begin{array}{ll} T_1 = F_0 - 5F_2 - 24F_4, & T_2 = F_0 - 8F_2 - 9F_4, \\ T_1^1 = F_0 + 4F_2 - 69F_4, & A_2 = F_0 - 8F_2 - 9F_4. \end{array}$$

Thus in the case of the strong field the states arising from the configuration  $(T_2)^1(E)^1$  are separated by an interval of  $12(F_2 - 5F_4)$ .

We can deduce the corresponding separations in the excited states arising from  $(T_2)^2(E)^1$  of  $\text{Cr}^{+++}$  and  $(T_2)^5(E)$  of  $\text{Co}^{+++}$  from the previous result, since these configurations may be considered as derived from  $(T_2)^3(E)^1$  and  $(T_2)^6(E)^1$  by the removal of a single electron from the  $T_2$  orbitals. The separation will still be  $12(F_2 - 5F_4)$ , but the order of the states will now be inverted, *i.e.*, the  $T_1^1$  state is the lower.

The effect of an axial field is found by using the operator  $(L_{z_1}^2 + L_{z_2}^2 - 4)$  in place of the potential  $(3z_1^2 + 3z_2^2 - 2r^2)$  of the two electrons. We find that for the  $T_2$  level this operator has no non-vanishing matrix elements, while for the  $T_1^1$  level

$$\begin{aligned} \langle ce|L_{z_1}^2 + L_{z_2}^2 - 4|ce\rangle &= 4 \\ \langle \frac{1}{2}b(\sqrt{3}d - e)|L_{z_1}^2 + L_{z_2}^2 - 4|\frac{1}{2}b(\sqrt{3}d - e)\rangle \\ &= \langle \frac{1}{2}a(\sqrt{3}d + e)|L_{z_1}^2 + L_{z_2}^2 - 4|\frac{1}{2}a(\sqrt{3}d + e)\rangle = -2 \end{aligned}$$

Hence we would predict a splitting of the lower level in  $\text{Cr}^{+++}$  and  $\text{Co}^{+++}$  in the presence of an axial field.

The case of the intermediate field is considered for  $\text{V}^{+++}$ . The calculation is most easily carried out by using the eigen-functions of the strong-field case as a basis. The matrix element between  $T_1$  and  $T_1^1$  due to the electrostatic interaction of the electrons is  $6(F_2 - 5F_4)$ . If we denote the total splitting of the  $d$ -orbital shell in the cubic field by  $5A$ , then the matrix determining the energy levels is

$$\begin{vmatrix} F_0 - 5F_2 - 24F_4 - 4A & 6(F_2 - 5F_4) \\ 6(F_2 - 5F_4) & F_0 + 4F_2 - 69F_4 + A \end{vmatrix}$$

The energy values used in Fig. 3 are obtained from this matrix.